THE INTERRELATIONSHIP BETWEEN VARIOUS FLOWS IN A CONDUCTING SYSTEM

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We prove a general theorem on the nature of the interrelationship between flows generated by a single force.

The results [1] derived earlier with respect to the interrelationship between various processes in a conducting system are generalized here for the case of an arbitrary number of co-current flows [1]. For the sake of convenience in dealing with the material, we will examine only a discrete system; however, all subsequent considerations may be appropriately referred to a continuous system.

We will proceed from the statements of nonequilibrium thermodynamics. Adopting the usual notation, we will write the linear relationship and the expression for the per-second increment in enthalpy in the following form:

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \qquad (i = 1,\ 2,\ \ldots,\ n), \tag{1}$$

$$\sigma = \sum_{i=1}^{n} J_i X_i. \tag{2}$$

If the flows and forces operative in (1) are independent (any other case can be reduced to this case), according to the general theory [2] we then have

$$|L_{ij}|_2^n = \begin{vmatrix} L_{22} & L_{23} & \cdots & L_{2n} \\ L_{32} & L_{33} & \cdots & L_{3n} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ L_{n2} & L_{n3} & \cdots & L_{nn} \end{vmatrix} \neq 0.$$

We can therefore express J_1 in terms of X_1 and all of the remaining flows are given by

$$J_1 = \varkappa X_1 + \sum_{i=2}^{n} Q_i J_i, \tag{3}$$

where $\varkappa$ and Q_i are certain functions of the phenomenological coefficients; Q_iJ_i expresses the fraction added to the magnitude of the flow J_1 by the flow J_i over and above the values generated directly by the force X_1; $\sum_{i=2}^{n} Q_iJ_i$ represents the total addition to J_1 by the entire set of flows $J_2,\ J_3,\ \ldots,\ J_n$. If $X_1 \neq 0$, and $X_2 = X_3 = \ldots = X_n = 0$, J_1 is the main flow, with the remaining flows representing the co-current flows.

Let us now compare two discrete systems with various matrices of phenomenological coefficients, but with identical values of $\varkappa$. When the force X_1 is acting in one of these systems and generates only the main flow J_{1I}, and if in the second system, in addition to the main flow J_{1II}, we have the co-current flows, then

$$J_{1II} > J_{1I}. \tag{4}$$

This confirms that the very appearance of the set of co-current flows serves to enlarge the main flow.

We will prove the validity of inequality (4). With this purpose in mind, let us examine two states of the second system, in one of which only the force X_1 is effective, while in the second to that force we add

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the forces $X_2, X_3, \ldots, X_n$ such that $J_2 = J_3 = \ldots = J_n = 0$. It is always possible to choose such forces, since $|L_{ij}|_2^n \neq 0$.

Let J'_{1II} be the J_1 flow in the second state. Then, according to (3), we have

$$J_{1I} = J'_{1II}. \tag{5}$$

We can apply the Prigogine general theorem on the minimum per-second increment in entropy [3, 4] to the state of the second system (which we are examining here). The conditions of its applicability are satisfied because X_1 is constant for these states and in one of these the flows $J_2, J_3, \ldots, J_n$ disappear. If σ_{II} and σ'_{II} correspond to the first and second states, we have

$$\sigma_{II} > \sigma'_{II}. \tag{6}$$

It follows from (2) that

$$\sigma'_{II} = J'_{1II} X_1, \tag{7}$$

$$\sigma_{II} = J_{1II} X_1, \tag{8}$$

since in the first case all of the flows with the exception of J_1 are equal to 0, while in the second case all of the forces with the exception of X_1 vanish. Comparing (8), (7), (6), and (5), we derive (4).

Let us clarify the proved statement with a simple example. For system II we will choose the membrane separating a multicomponent flowing medium into two homogeneous parts; the membrane is permeable to the particles of this medium. Let $X_1 = \Delta T/T^2$ and J_1 is the flow of heat. We will assume that the heat flow through the membrane is interrelated with the flows of matter. If we know the phenomenological coefficients, we can calculate $\varkappa_{II}$ from the formula

$$\varkappa = \frac{|L_{ij}|_1^n}{|L_{ij}|_2^n},$$

which follows from (3) and (1). We can also find the value of $\varkappa$ experimentally, on the basis of the determining equation (3).

System I is obtained if, instead of the membrane, we use a plate that is impermeable to matter. In this case, $\varkappa_I = L_{1I}$. As is well known [2], $L_{11} = \lambda T^2 s/d$. Knowing $\varkappa_{II}$ and λ, we can easily choose the plate dimensions so that at the test temperature T we satisfy the condition $\varkappa_{II} = \varkappa_I$. On the basis of the statement which we have proved, we can state that when identical forces X_1 are active, the heat flow through the membrane is greater than the flow of heat through the plate. This difference is brought about as a consequence of the fact that co-current flows are set up within the membrane, whereas no such flows are present in the plate.

Let us now examine the special case in which the co-current flows are not related to each other, i.e., the case in which

$$L_{ij} = 0 \quad (i, j = 2, 3, \ldots, n) \quad \text{when } i \neq j. \tag{9}$$

This limitation is imposed on these systems in addition to the conditions which were indicated in the formulation of the general theorem.

Let there be a complete set of co-current flows $J_{2II}, J_{3II}, \ldots, J_{nII}$ in the second system, and let one of these flows, J_k for example, be missing from the first system. More accurately, $J_{iI} = J_{iII}$, if $1 \neq i \neq k$ and $J_{kII} \neq J_{kI} = 0$. We will then again satisfy the relationship

$$J_{1II} > J_{1I}.$$

Indeed, we can examine the two states of the second system, in one of which we have only the force X_1, while in the second state the force X_k is added to the first, so that $J'_{kII} = 0$. As a consequence of (9) the addition of X_k will change the magnitudes of the remaining co-current flows and, consequently,

$$J'_{iII} = J_{iII} = J_{iI} \qquad (1 \neq i \neq k).$$

Here we can apply the Prigogine theorem with respect to the constant forces X_i ($i \neq k$) and to the disappearing flow J_k. We will eventually come to relationships analogous to (6), (7), and (8), and considering (10), we will achieve the required inequality $J_{1II} > J_{1I}$.

Now, however, as follows from (10), the difference between J_{1I} and J_{1II} is governed exclusively by the flow J_k. This means that in this case each co-current flow is generated independently of the others and is oriented so as to intensify the main flow J_1.

In conclusion, we note that our results could have been obtained in another way, proceeding directly from the properties of the quadratic forms and the corresponding matrices. However, this would have required more complex approaches and would have taken up considerably more space. Haase used this method to compare the coefficients of thermal conductivity with and without the presence of mass transfer [2]. His relationship is derived directly from (4) and (5), if J_1 in the latter is understood to refer to the heat flow.

NOTATION

$\varkappa_{II}$ and $\varkappa_I$ are the values of $\varkappa$ for the membrane and the plate, respectively;
$|L_{ij}|_1^n$ is the determinant of the matrix of the phenomenological coefficient;
T is the average value of the temperature for the two sides of the membrane or the plate;
ΔT is the temperature difference (small in comparison with T) between the two sides of the membrane or of the plate;
d and s are the thickness and cross-sectional area of the plate;
λ is the coefficient of thermal conductivity for the plate at the temperature T.

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